LIQUEFACTION CO-PROCESSING
OF COAL AND SHALE OIL

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ABSTRACT

Results are reported for a series of experiments in which Wyodak subbituminous coal
and shale oil derived from medium grade Colorado shale were co-processed at typical
coal liquefaction reaction conditions.  Distillate yields in excess of 60 wt% MAF
coal with corresponding hydrogen consumption values of less than 2.8 wt% MAF coal
were obtained in a once-through process configuration.  Encouraging results were
also obtained from low severity experiments using $CO/H_2O$ rather than $H_2$ as reducing
agent.  Prehydrotreatment of the shale oil, feed coal reactivity, and use of a
disposable catalyst were shown to affect process performance.

INTRODUCTION

A number of studies have been reported in which coal and non-coal-derived heavy
solvents were simultaneously converted to more valuable distillable liquid products
(1 - 6).  This type of once-through process, known as co-processing or liquefaction
co-processing, has several potential advantages over conventional direct liquefac-
tion:

- Two low grade feeds are converted to higher quality liquid products.

- Recycle solvent requirements are reduced or eliminated resulting in lower
  capital investment and operating costs.

- Existing petroleum refinery capacity can be utilized with minimal process
  modification.

However, liquefaction co-processing does suffer from a number of technical problems
which must be solved before commercial development can proceed.  Most non-coal-
derived heavy oils derived from petroleum, oil shale, or tar sands are less aro-
matic than coal-derived liquids, and, not surprisingly, have been shown to be
rather poor coal dissolution solvents.  Typically, very severe thermal reaction
conditions and/or use of expensive heterogeneous catalysts are utilized during
co-processing to obtain sufficiently high levels of coal conversion.  This general-
ly results in excessive hydrogen consumption and cracking of distillable liquids to
gases.

An alternate approach to the problem of increasing coal dissolution has been
employed in the present study.  Results of exploratory liquefaction co-processing
experiments demonstrated that selected non-coal-derived heavy oils, each with a
nitrogen content in excess of about 1.2 wt%, could be used to dissolve Wyodak
subbituminous coal at typical coal liquefaction reaction conditions (7).  This
effect was not surprising, since quinoline-type nitrogen compounds such as tetrahy-
droquinoline (THQ) have been shown to greatly enhance coal dissolution in model
compound studies (8 - 10).  Based on encouraging results from the exploratory
screening runs, additional co-processing studies using promising coal/heavy oil
combinations were undertaken.

The objective of this paper is to report yield and conversion results from lique-
faction co-processing experiments using Wyodak subbituminous coal and shale oil

derived from medium grade Colorado shale. Runs designed to demonstrate the effects of feed coal reactivity, mild hydrotreatment of feed shale oil prior to co-processing, and use of hydrogen or carbon monoxide/water as feed gas were included in this study.

EXPERIMENTAL PROCEDURE

Wyodak subbituminous coal samples Wyo-1 and Wyo-3 were used as feed coals in the liquefaction co-processing experiments. Ultimate analyses for these samples are presented in Table I. Sampling and preparation details of the coals have been reported elsewhere (11, 12). Previous reactivity studies performed on four Wyodak subbituminous coals including Wyo-1 and Wyo-3 indicated that Wyo-3 coal was an extremely reactive coal at representative direct liquefaction reaction conditions (11, 13). The high degree of reactivity was primarily attributed to the high organic sulfur and reactive maceral (vitrinite and exinite) contents of Wyo-3 coal. Wyo-1 coal was found to be much less reactive at liquefaction reaction conditions. Coal samples were dried to less than 1.0 wt% moisture content before use in the liquefaction co-processing experiments.

Two shale oil samples were used in the liquefaction co-processing runs. Solvent A-5 was a full boiling range sample of shale oil obtained from the Western Research Institute (formerly the Laramie Energy Technology Center of the Department of Energy). This sample was produced from thermal retorting of medium grade (29 gal/ton) Colorado oil shale. Solvent A-6 was prepared by mildly hydrotreating a portion of sample A-5 in a two liter batch Autoclave Magnedrive II reactor at 650°F for one hour with an initial cold hydrogen pressure of 2000 psig. Nalcomo 477 cobalt molybdate catalyst was used to hydrotreat the shale oil. Catalyst samples were thermactivated at 1000°F for two hours in a muffle furnace prior to use. Approximately 0.6 wt% hydrogen was consumed by the shale oil during hydrotreating. Properties of shale oil samples A-5 and A-6 are presented in Table II. Approximately 50 wt% of the nitrogen in these samples existed in quinoline-type or hydroquinoline-type molecular structures.

Iron oxide provided by the Kerr-McGee Corporation and carbon disulfide were used as disposable catalysts in some co-processing runs using hydrogen as feed gas. Each of these materials was added to the reaction mixture in an amount equal to 5 wt% of the dry feed coal. Iron sulfate (5 wt% MF feed coal) was used as catalyst in selected $CO/H_2O$ experiments.

The liquefaction co-processing experiments were carried out in a 60 cm³ stirred microautoclave reactor system designed and constructed at the University of Wyoming. The reactor was similar to larger Autoclave batch reactors except that heating was accomplished with an external high temperature furnace. At the end of each run, the reactor and its contents were quenched with an icewater batch. This reactor system provided the benefits of small tubing bomb reactors [quick heatup (~2 min. from room temperature to 850°F) and cooldown (~30 sec. back to room temperature)], while at the same time insuring sufficient mechanical agitation of the reactants with an Autoclave Magnedrive II stirring assembly to minimize hydrogen mass transfer effects. The system was also designed so that the reactor pressure was very nearly constant throughout an experiment. Two iron-constantan thermocouples attached to a Fluke 2175A digital thermometer were used for temperature measurements. One thermocouple measured the temperature of the reactor contents, while the other measured the temperature of the reactor wall. Reactor pressure was monitored using a 0 - 5000 psi Marsh pressure gauge.

A majority of the liquefaction co-processing runs were completed at representative coal liquefaction reaction conditions: 825°F reaction temperature, 2000 psig initial cold hydrogen pressure, and 30 or 60 minutes reaction time. Some preliminary experiments were also completed at more mild reaction conditions using carbon

monoxide and water rather than hydrogen as the reducing agent. In these runs, hydrogen was produced from CO and $H_2O$ via the water gas shift reaction. The $CO/H_2O$ runs were completed at 600°F reaction temperature, 1500 psig initial cold carbon monoxide pressure, and 30 minutes reaction time. Distilled water in an amount equal to 50 wt% of the dry feed coal was added to runs using a carbon monoxide atmosphere.

Gaseous products were analyzed using gas chromatography. Water and distillate yields were measured by distilling portions of the combined liquid-solid product mixture to an 850°F endpoint in a microdistillation apparatus. Additional portions of the liquid-solid product mixture were extracted in a Soxhlet extraction apparatus using cyclohexane, toluene, and pyridine. Details of the experimental procedures used in this work have been reported (7).

RESULTS AND DISCUSSION

Using data collected with the analytical procedures described, detailed yield and conversion results were computed for each liquefaction co-processing run. Details of the computational methods used in this study have been described previously (7). For purposes of the present discussion, process performance will be monitored using the following three parameters: $C_4$-850°F distillate yield (wt% MAF coal basis), hydrogen utilization efficiency, and pyridine conversion (wt% MAF basis). Hydrogen utilization efficiency is defined as the mass of $C_4$-850°F distillate produced per unit mass of hydrogen consumed. The value of this parameter provides a good indication of the overall efficiency of hydrogen consumed in the co-processing experiments. Pyridine conversion is defined as a measure of the extent of conversion of all feeds (coal and non-coal-derived heavy oil) to pyridine soluble products. However, since both A-5 and A-6 shale oil samples were completely soluble in pyridine, the pyridine conversion values reported in this paper are direct measures of the extent of coal conversion in the co-processing runs.

Effect of Shale Oil Prehydrotreatment

The results from liquefaction co-processing experiments using Wyo-3 coal and A-5 or A-6 shale oil at 825°F and 2000 psig initial cold hydrogen pressure are shown in Figures 1 - 3. It is apparent from this data that mild prehydrotreatment of the shale oil prior to co-processing greatly enhances process performance. Distillate yields of 55 - 60 wt%, hydrogen utilization efficiencies of about 20, and pyridine coal conversion values of 68 - 85 wt% were obtained using Wyo-3 coal and A-6 shale oil. Similar enhancement effects were seen using Wyo-1 feed coal. Previous co-processing studies by Kerr-McGee using Ohio No. 5 bituminous coal and Canadian Cold Lake bitumen also demonstrated the beneficial effect of heavy oil hydrotreatment prior to co-processing (14).

At least two possible reasons exist for the effects shown in Figures 1 - 3. First, mildly hydrotreated A-6 shale oil acted as a more powerful hydrogen donor solvent than A-5 in promoting coal conversion and distillate production. Secondly, the quinoline-type nitrogen content of A-5 was approximately 0.7 wt%. Mild hydrotreatment of A-5 presumably converted a number of the quinoline structures to hydroquinoline structures. As mentioned earlier in this paper, hydroquinolines such as tetrahydroquinoline (THQ) have been shown to actively promote coal solvation in direct liquefaction. The data shown in Figures 1 - 3 suggest that a similar effect occurred during liquefaction co-processing with A-6 shale oil.

Effect of Feed Coal Reactivity

Figure 4 presents a comparison of yield results for co-processing runs using Wyo-1 and Wyo-3 coal. These data show that liquefaction co-processing performance is a strong function of feed coal reactivity as measured by the extent of dissolution to

pyridine solubles and distillate production. As shown in Figure 5, the detrimental effects of low feed coal reactivity can be partially offset by use of a disposable catalyst such as iron oxide/carbon disulfide.

## Liquefaction Co-Processing Using Carbon Monoxide and Water

Several previous studies have reported the successful liquefaction of low rank coal at mild reaction conditions using carbon monoxide and water in place of hydrogen gas (5, 15, 16). In these runs, hydrogen was provided by the water gas shift (WGS) reaction involving carbon monoxide and water. In the aqueous phase, a number of catalysts such as alkali metal salts, alkaline earth salts, and organic nitrogen bases have been shown to catalyze the WGS reaction (17).

Hypothesizing that the high basic nitrogen content of A-6 shale oil would also catalyze the WGS reaction, several preliminary liquefaction co-processing experiments using Wyo-3 coal, A-6 shale oil, and $CO/H_2O$ were completed. As shown in Figure 6, significant conversion of coal and 850°F+ shale oil to distillate liquids was obtained, even though the reaction conditions were very mild. Use of iron sulfate as a disposable catalyst provided some improvement in yield structure and coal conversion. Based on these encouraging results, a more extensive study of liquefaction co-processing using carbon monoxide and water is underway.

CONCLUSIONS

A series of liquefaction co-processing experiments has been completed using two Wyodak subbituminous coals and two shale oil feeds. Both hydrogen and carbon monoxide/water were evaluated as reducing agents. Results indicated that prehydrotreatment of the shale oil, feed coal reactivity, and to some extent, use of a disposable catalyst all affect process performance. Sample A-6 was found to be an attractive feedstock for liquefaction co-processing. Distillate yields in excess of 60 wt% MAF coal were obtained using Wyo-3 coal and A-6 shale oil at typical coal liquefaction conditions. Encouraging results were also obtained using $CO/H_2O$ at much more mild reaction conditions.

ACKNOWLEDGEMENTS

REFERENCES

1.  Yan, T.Y., and Espenscheid, W.F., Fuel Proc. Tech., 7, 121, (1983).

2.  Shinn, J.H., Dahlberg, A.J., Kuehler, C.W., and Rosenthal, J.W., "The Chevron Co-Refining Process," Proceedings of the Ninth Annual EPRI Contractors' Conference on Coal Liquefaction, Palo Alto, California, (May 1984).

3.  Kelly, J.F., Fouda, S.A., Rahimi, P., and Ikura, M., "CANMET Coprocessing: A Status Report," CANMET Coal Conversion Contractors' Review Meeting, Calgary, Alberta, Canada, (November 1984).

4.  Curtis, C.W., Guin, J.A., Pass, M., and Tsai, K.J., ACS Fuel Chem. Preprints, 29, 5, 155, (1984).

5.  Ignasiak, B., Kovacik, G., Ohuchi, T., Lewkowicz, L., and duPlessis, M.P., "Two-Stage Liquefaction of Subbituminous Alberta Coals in Non-Donor Solvents," CANMET Coal Conversion Contractors' Review Meeting, Calgary, Alberta, Canada, (November 1984).

6.  Miller, R.L., "Use of Non-Coal-Derived Heavy Solvents in Direct Coal Liquefaction," Proceedings of the Tenth Annual EPRI Contractors' Conference on Coal Liquefaction, Palo Alto, California, (April 1985).

7.  Miller, R.L., "Use of Non-Coal-Derived Heavy Solvents in Direct Coal Liquefaction," Interim Report for EPRI Project RP 2383-01, (November 1985).

8.  Atherton, L.F., and Kulik, C.J., "Advanced Coal Liquefaction," presented at the 1982 AIChE Annual Meeting, Los Angeles, California, (November 1982).

9.  McNeil, R.I., Young, D.C., and Cronauer, D.C., Fuel, 62, 806, 1983.

10. Broderick, T.E., "Liquefaction of Wyodak Coal in Tetrahydroquinoline," M.S. Thesis, University of Wyoming, Laramie, Wyoming, (1984).

11. Miller, R.L., "Effect of Wyodak (Wyoming) Coal Properties on Direct Liquefaction Reactivity," Ph.D. Dissertation, Colorado School of Mines, Golden, Colorado, (1982).

12. Silver, H.F., Corry, R.G., and Miller, R.L., "Coal Liquefaction Studies," Final Report for EPRI Projects RP 779-23 and RP 2210-1, (December 1982).

13. Miller, R.L., and Baldwin, R.M., Fuel, 64, 1235, (1985).

14. Rhodes, D.E., "Comparison of Coal and Bitumen-Coal Process Configurations," Proceedings of the Tenth Annual EPRI Contractors' Conference on Coal Liquefaction, Palo Alto, California, (April 1985).

15. Ross, D.S., Blessing, J.E., Nguyen, Q.C., and Hum, G.P., Fuel, 63, 1206, (1984).

16. Hodges, S., and Creasy, D.E., Fuel, 64, 1229, (1985).

17. Elliott, D.C., and Sealock, L.J., I & EC Proc. Des. Dev., 22, 426, (1983).

## Table I

### Ultimate Analysis of Wyodak Subbituminous Coal Samples

| Sample | Wyo-1 | Wyo-3 |
|---|---|---|
| **Ultimate Analysis, wt% dry basis** | | |
| Carbon | 69.8 | 58.2 |
| Hydrogen | 4.7 | 4.3 |
| Nitrogen | 0.8 | 0.8 |
| Sulfur | 0.3 | 2.9 |
| Sulfate | 0.0 | 0.8 |
| Pyrite | 0.0 | 0.9 |
| Organic | 0.3 | 1.2 |
| Oxygen (difference) | 18.3 | 13.9 |
| Ash | 6.1 | 19.9 |

## Table II

### Properties of Shale Oil Samples

| Sample | A-5 | A-6 |
|---|---|---|
| **Wt% Distilled** | | |
| Water | 0.7 | 0.1 |
| 350°F | 4.2 | 10.3 |
| 350°-500°F | 9.6 | 18.3 |
| 500°-650°F | 18.8 | 22.5 |
| 650°-850°F | 39.0 | 29.8 |
| 850°F+ | 27.7 | 19.0 |
| **Ultimate Analysis, wt% dry basis** | | |
| Carbon | 83.3 | 84.7 |
| Hydrogen | 12.1 | 12.9 |
| Nitrogen | 1.4 | 1.2 |
| Sulfur | 0.5 | 0.4 |
| Oxygen (difference) | 2.7 | 0.8 |
| Ash | 0.0 | 0.0 |
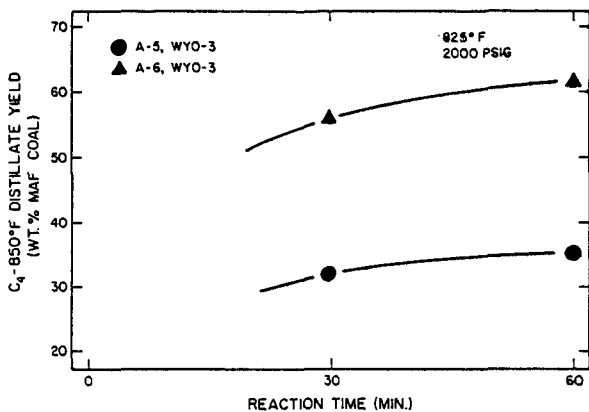
Figure 1. Distillate Yield as a Function of
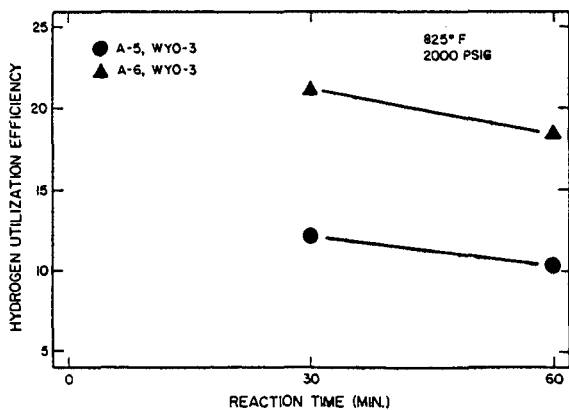Reaction Time and Shale Oil Feed



Figure 2. Hydrogen Utilization Efficiency as a
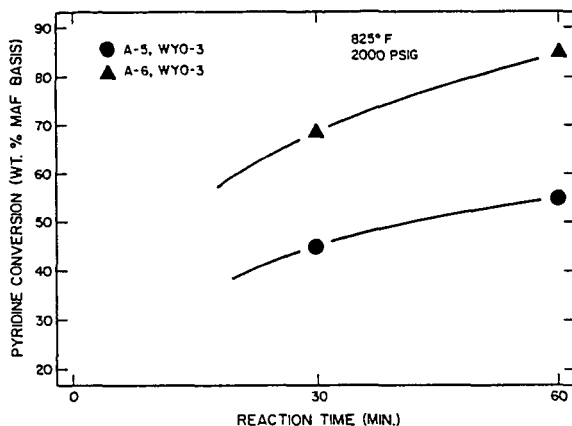Function of Reaction Time and Shale
Oil Feed

Figure 3. Pyridine Conversion as a Function of Reaction Time and Shale Oil Feed
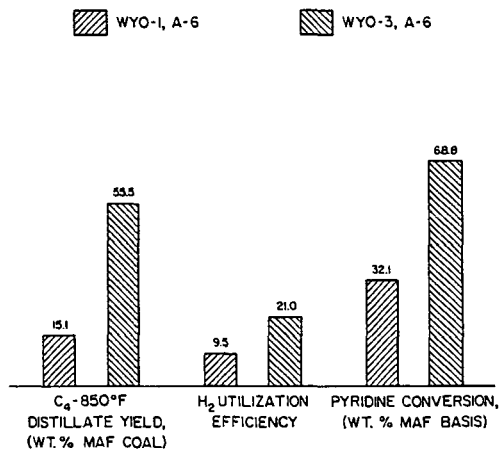


Figure 4. Effect of Feed Coal Reactivity on Process Performance (Reaction Conditions: 825°F, 2000 psig $H_2$, 30 min.)
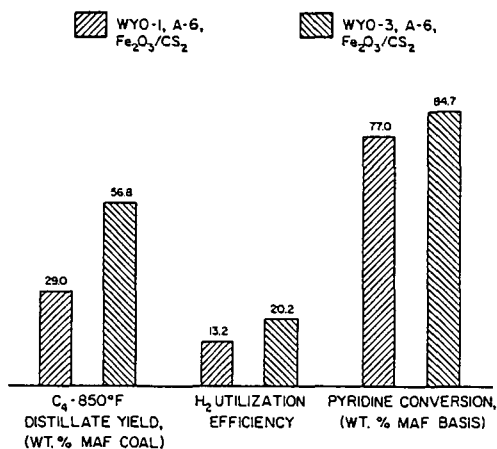
Figure 5.  Effect of Feed Coal Reactivity on
Process Performance (Reaction Conditions:  825°F, 2000 psig $H_2$, 30
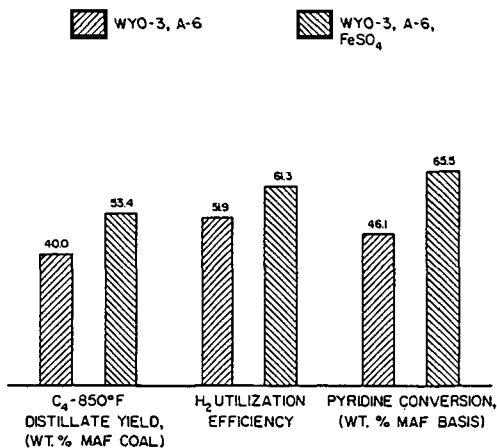min., $Fe_2O_3/CS_2$ Catalyst)



Figure 6.  Liquefaction Co-Processing Yield
Results using Carbon Monoxide/
Water (Reaction Conditions:  600°F,
1500 psig CO, 30 min.)